

**XAFS Study of the Binding Mechanism of Contaminant Anions to Self-Assembled Monolayers on Mesoporous Supports**

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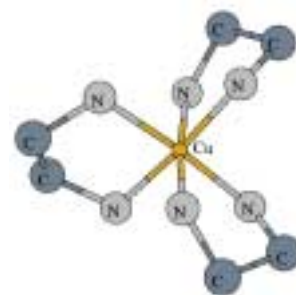
Beamline(s): X23A2

**Introduction:** Groundwater contamination by geologic arsenic has recently become a great concern in many parts of the world [1-4]. The use of arsenic and chromium in an array of agricultural and industrial processes has also resulted in groundwater contamination of many industrial sites [5]. Unfortunately, most anion exchange methods use quaternary ammonium salts that have little, if any, interaction between the cation-anion pair, and thus selectivity is poor. In complex groundwater matrices many ubiquitous anions such as sulfate are present at higher concentrations than the target contaminants. Therefore, the current anion exchange methods with their lack of selectivity are inefficient. In recent years, self-assembled monolayers on mesoporous supports (SAMMS) have been found to be superior sorben materials for the sequestration of heavy-metal cations. Molecular self-assembly enables direct introduction of a variety of useful chemical interfaces, and subsequent synthetic elaboration of the monolayer foundation permits virtually unlimited interfacial design. A recently article [6] reported the synthesis of SAMMS lined with cationic metal complexes as a novel anion-binding materials. In the presence of comparatively high concentrations of sulfate, these metallated SAMMS materials --incorporating a monolayer of ethylenediamine (EDA) ligands bound to the mesoporous silica with three EDA ligands chelated to a central Cu(II) ion-- can remove arsenate and chromate very effectively from solutions containing typical groundwater concentrations of toxic oxometallate anions. To improve and expand the selectivity of the SAMMS materials, we must understand the interfacial chemistry. Therefore, we have undertaken a detailed XAFS study of the Cu, As, and Cr environments in these materials.

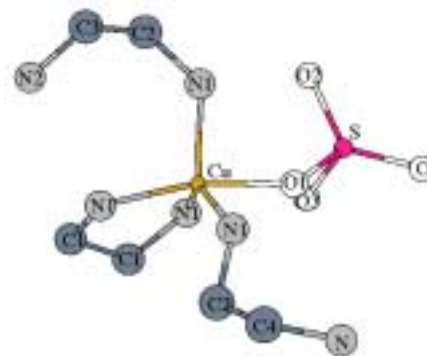
**Methods and Materials:** A complete description of the synthesis of the SAMMS samples is in Ref. [6]. Four SAMMS samples were investigated in this study. Sample A was not loaded with anions. Samples B, C, and D were loaded with  $\text{SO}_4$ ,  $\text{SO}_4$  and  $\text{AsO}_4$ , and  $\text{SO}_4$  and  $\text{CrO}_4$ . Transmission XAFS data were collected at beamline X23A2 at the NSLS. Cu K-edge data were collected for samples A, C, and D samples at 100 K and for sample B at room temperature. Cr K-edge data were collected for sample C, and As K-edge data were collected for sample D at room temperature and 100 K. The fine-grained powder samples were packed in Kapton tape. A fixed-exit double-crystal silicon [220] monochromator was used to select the X-ray energy. The appropriate gas mixture was used to achieve 10-15% adsorption in the incident X-ray ion chamber, and argon gas was used in the transmission ion chamber. Linearity testing indicated less than 0.5% nonlinearity in the incident X-ray intensity for 50% attenuation. All of the measurements were made at least twice, and the resulting chi data were averaged.

**Results:** Fit results from sample A indicate that the Cu(II) ions are coordinated with three chelating EDA ligands with octahedral symmetry (see Figure 1). Fit results for samples B, C, and D indicate that the tetrahedral anions share one of the tetrahedral oxygen atoms directly with the Cu(II), forming an inner-sphere monodentate complex. During the binding process two secondary amine groups of two EDA ligands are displaced, resulting in a Cu(II) with a trigonal bipyramidal geometry (see Figure 2). Confidence in the model is based on three factors: (1) Statistically, the fit to the data is better than for any of the other 15 models tested. (2) The fit parameters are reasonable. (3) This model is one of the lowest-energy configurations formed in molecular modeling studies using PC Spartan [6].

**Conclusions:** During the process of binding, the Cu center undergoes a geometry change from octahedral to trigonal bipyramidal. The loss of symmetry that accompanies this geometry change alleviates any orbital degeneracy, thereby enhancing the stability of the interfacial complex. This enhanced stability, coupled with the lack of dissociation observed with the contaminant anions, suggests that the laden SAMMS evaluated may very well have excellent long-term stability as waste forms.



**Figure 1.** Structure of Cu in the SAMMS. The octahedral complex is formed from three EDA ligands about a Cu(II) ion. Each C or N has two closely bound H atoms that are not shown for simplicity.



**Figure 2.** Structure of Cu in the laden SAMMS. Each C or N has two closely bound H atoms that are not shown for simplicity.

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